IASWS • SPECIAL ISSUE

Lead mobilisation in the hyporheic zone and river bank sediments of a contaminated stream: contribution to diffuse pollution

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Abstract

Purpose Past metal mining has left a legacy of highly contaminated sediments representing a significant diffuse source of contamination to water bodies in the UK and worldwide. This paper presents the results of an integrated approach used to define the role of sediments in contributing to the dissolved lead (Pb) loading to surface water in a mining-impacted catchment.

Materials and methods The Rookhope Burn catchment, northern England, UK, is affected by historical mining and processing of lead ore. Quantitative geochemical loading determinations, measurements of interstitial water chemistry from the stream hyporheic zone, and inundation tests of bank sediments were carried out.

Results and discussion High concentrations of Pb in the sediments from the catchment, identified from the British Geological Survey (BGS) Geochemical Baseline Survey of the Environment (GBASE) data, demonstrate both the impact of mineralisation and widespread historical mining. The results from stream water show that the stream Pb load increased in the lower part of the catchment, without any apparent or significant contribution of point sources of Pb to the stream. Relative to surface water, the interstitial water of the hyporheic zone contained high concentrations of dissolved Pb in the lower reaches of the Rookhope Burn catchment, downstream of a former mine washing plant. Concentrations of 56 $\mu g\ l^{-1}$ of dissolved Pb in the interstitial water of the hyporheic zone may be a major cause of the deterioration of fish habitats in the stream and be regarded as a serious risk to the target of good ecological status as defined in the European Water Framework Directive. Inundation tests provide an indication that bank sediments have the potential to contribute dissolved Pb to surface water.

Conclusions The determination of Pb in the interstitial water and in the inundation water, taken with water Pb mass balance and sediment Pb distribution maps at the catchment scale, implicate the contaminated sediments as a large Pb supply to surface water. Assessment of these diffuse contaminant sources is critical for the successful management of mining-impacted catchments.

Keywords Abandoned mines • Diffuse pollution • G-BASE • Hyporheic zone • Inundation test • Northern Pennines, UK • Pb • Sediments

1 Introduction

The importance of diffuse pollution sources in abandoned mine-impacted river catchments and their potential to affect water quality and ecology has been fully recognised (Caruso and Ward 1998; Kimball et al. 2002; Balistrieri et al. 2007; Mayes et al. 2008; Mighanetara et al. 2009; Banks and Palumbo-Roe 2010; Gozzard et al. 2011). These dispersed sources of acidity and dissolved metal load to surface water arise from seepage and runoff from mine waste, contaminated groundwater inputs through the hyporheic zone and remobilization of previously deposited metal-rich particles in stream channels and floodplains. As such, they pose considerable barriers to compliance with the demands of the EU Water Framework Directive (WFD) and represent a major management issue for the mining industry worldwide (Baresel et al. 2007; Coetser et al. 2007). Failing to account for these dispersed sources of pollutant loading in a catchment can severely reduce the effectiveness of point source remediation directed to the treatment of mine water discharges.

Past mining operations in England and Wales (UK) have left a substantial legacy of highly contaminated sediments in rivers that extend many kilometres downstream of the mines (Macklin et al. 2006). The erosion, transport and deposition of historically contaminated alluvium are very important sources of sediment-borne metals in all mining-affected river systems in England and Wales (Hudson-Edwards et al. 2008). Re-suspension of these sediments during floods has the potential to cause additional harm to aquatic life, and to contaminate floodplain soils used for agriculture. Furthermore, the changes in water chemistry following the remediation of mine drainage sources could result in an enhanced release and remobilisation of metals from the sediments (Butler 2009). However, few attempts have been made to determine the fluxes of metals to surface water associated with contaminated sediments. This paper describes the role of sediments in contributing to the loading of dissolved Pb to surface water in the Rookhope catchment, northern England. The catchment has been affected by historical mining and processing of lead (Pb) and zinc (Zn) ore and is representative of several catchments affected by the environmental legacy related to mining in the Northern Pennine Orefield, northern England. The catchment has recently been highlighted in a national review as one of the most severely mine-impacted (in terms of water quality) in England and Wales (Mayes et al. 2009).

In order to estimate the sediment contribution to the diffuse dissolved Pb loading in the catchment waters, the investigation consisted of three parts: i) quantification of the diffuse dissolved metal load along the stream using a chemical mass balance approach; ii) collection of evidence of the sediment contribution to the diffuse load by sampling bed sediments and sediment interstitial water in the hyporheic zone of the stream; and iii) laboratory inundation tests of the river bank sediments.

2 Study site

The Rookhope Burn catchment in County Durham, Weardale, occupies an area in the order of 37 km^2. The southerly flowing stream contributes a discharge ranging from 100 to 2300 $l\ s^{-1}$ to the River Wear at Eastgate

(Fig. 1). The annual effective rainfall is in the order of 1000 mm, with monthly contributions varying between 53 and 116 mm. Flow conditions in the stream give rise to a flashy hydrograph and storm events are transmitted rapidly through the catchment.

The upper part of the Rookhope Burn catchment has been incised in Namurian sandstones and mudstones of the Stainmore Formation (Yoredale Group). Its source is in grouse moorlands at an elevation of about 600 m Ordnance Datum (OD). The middle portion of the catchment comprises a relatively treeless landscape characteristic of the mining heritage of the area and is largely utilised for hill farming. The bedrock in this part of the catchment comprises the interbedded shales and sandstones of the lower part of the Stainmore Formation. Evidence of the former mining comes from: the scars of abandoned quarries, formerly exploited for iron ore and building stone; galena and fluorspar mines, that occur in the rakes and flats; piles of mine waste; abandoned mine buildings; and former tailings lagoons. The mine workings extend into the lower part of the catchment, but here they are interspersed with karst features including dolines and springs, which have developed in the limestones of the basal part of the Stainmore Formation. The more resistant Alston Formation bedrock (basal formation of the Yoredale Group) gives rise to a number of waterfalls towards the base of the catchment, which contrasts with the karstic nature of the till-covered limestones immediately to the north.

Superficial deposits and mine-reworked sediments are distributed widely throughout the channel, with only local outcrops of bedrock in the bed of the stream. To date, no detailed geomorphological studies of the catchment have been undertaken. However, both field evidence and studies of historic maps of an adjacent catchment (Swinhope Burn; Warburton et al. 2003) would suggest that stretches of the stream channel with a low gradient may change in response to floods and changes in sediment supply. There is also evidence of bank instability alongside specific stretches of the stream. Another source of potential instability is mine outbursts, resulting from underground collapse. Sediment mobilisation can be important in exposing fresh minerals to weathering (Hudson-Edwards et al. 2008)

3 Methods

3.1 Surface water sampling and mass balance calculations

The surface water data include flow monitoring and chemical data for inflows and instream waters throughout the catchment (Fig. 1). Full description of the water sampling can be found in Banks and Palumbo-Roe (2010). Results from Banks and Palumbo-Roe (2010) are supplemented by a further sampling event (April 2009) and re-analysis of waters for Pb by Inductively Coupled Plasma Atomic Mass Spectrometry (ICP-MS). Re-analysis was undertaken as previous results by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) were reported at or around the ICP-AES method detection limit (0.010 mg l^{-1}). Chemical data and major physico-chemical parameters were used to calculate saturation indices (SI) for relevant mineral phases using PHREEQC (Parkhurst and Appello 1999) and the WATEQ4f database (Ball and Nordstrom 1991).

The surface water metal load distribution along the Rookhope Burn was calculated from the product of the flow and element concentration. Sources and sinks of dissolved Pb along the Rookhope Burn were determined using a mass balance approach. A mass balance determines the element that is gained or lost in a stream stretch by comparing the amount of the element that enters a stream segment with the amount that leaves the same segment, based on the assumption that the load at the end of a stream segment includes the load from the point upstream plus the contribution from all surface and subsurface inflows along the stream segment.

3.2 Sediments and sediment interstitial water sampling and analysis

The sampling locations were selected from the findings of the first phase of investigation (Banks and Palumbo-Roe 2010). Specific features associated with these locations are summarised in Table 1. Bed sediment samples were collected along the Rookhope Burn (see Fig. 1) during the week of May 11-15 2009, during low river flow conditions. Points HZ-0 and HZ-A0 represent two sampling sites not impacted by mining activities and each is characterised by a different underlying geology. Sediment chemical analysis on the <150µm fraction was carried out using mixed acid digestion ($HF/HClO_4/HNO_3$) and ICP-AES. The pH was analysed by a $CaCl_2$/slurry method, organic matter content by loss-on-ignition (LOI) at 450°C, and mineralogical analysis using X-ray Diffraction (XRD).

At each location, the interstitial water from the hyporheic zone of the stream was collected using a low-flow inertial pump from a 50 mm diameter stainless-steel piezometer inserted 30 cm into the streambed sediments. The overlying surface water was also sampled at each sampling point. 0.45 µm filtered water samples, acidified to 1% HNO_3, were analysed by ICP-MS. The water pH and Eh were measured in the field using hand-held Hannah combination HI 9125 meters with associated probes. The Pt electrode Eh measured values were corrected to the Standard Hydrogen Electrode.

Additionally, 41 sediment Pb analyses were retrieved from the British Geological Survey (BGS) Geochemical Baseline Survey of the Environment (GBASE) database. Sediments were collected from the active drainage channel of first or second order streams as part of a national geochemical survey at a sampling density of one sample every 1-2 km^2 on average. G-BASE field procedures and sediment analysis are documented in Johnson et al. (2005).

3.3 Bank sediment inundation test

Duplicate samples of bank sediments were collected for sites HZ-11, HZ-16 and HZ-23. The Rookhope Burn stream water collected at the footbridge in the Rookhope village (co-ordinates 393750 542840) at the time of the sediment sampling was used to flood the sediments. The organic carbon concentration of the stream water sample, measured as non-purgeable organic carbon, was 2.57 mg l^{-1}, the pH was 7.82 and the Pb concentration was 0.7 µg l^{-1}.

About 50 g of each sediment sample was submerged with 500 ml of Rookhope stream water and inundated for a 3 month (88 day) period in a laboratory-scale inundation test. Filtered (0.45µm) samples of the overlying water column were collected at 1, 7, 28 60 and 88 days of inundation after gently stirring the inundation water without disturbing the sediment at the interface. These were analysed for major and trace anions and cations by ICP-MS. The pH and Eh of the inundation water were measured at the same time. The porewater for each replicate was collected for analysis by centrifugation at 3000 G at the conclusion of the 88 day inundation period.

4 Results and discussion

4.1 Surface water lead load distribution

Fig. 2 shows the Pb concentration profile along Rookhope Burn as dissolved Pb concentration in the surface water (µg l^{-1}) and Pb load (mg s^{-1}) for three sampling events. There were large differences in concentrations in the three sampling events, but similar patterns across the catchment. The greatest increase in the dissolved Pb concentration (see Fig. 2) occurred from the headwaters to point 3, downstream of Grove Rake Mine (the last lead and fluorspar workings to close in 1999; Johnson and Younger 2002). Farther down the catchment, dissolved Pb displayed lower concentrations.

The Pb load profile displayed discrete peaks, for all three sampling events, partly in response to visible point contributions from mine waters and seepage from mine spoils (see Fig. 2). In contrast with a commonly observed attenuation of dissolved metals downstream from the pollution source – due to dilution, dispersion, precipitation and adsorption processes (Chapman et al. 1983) – the Pb load steadily increased, generally from point 16 towards the lower part of the catchment. From sampling points 23 to 25, mass balance calculations (Table 2) indicated a net load increase ranging from 27% to 97% in the three sampling events (the variability of the load increase is attributed to antecedent conditions prior to the sampling events, with greater load increases occurring in response to rainfall events). In this lower part of the catchment, the influence of tributaries or point sources was found negligible in terms of metal load contribution, strongly suggesting a dispersed input of Pb.

4.2 Lead concentrations in bed sediments

The sediment mineralogical composition was dominated by the presence of quartz (c. 58–76%), with additional contributions from mica (c. 9–14%), fluorite (c. 2–12%), kaolin (c. 2–5%) and chlorite (c. 2–3%). Bank and bed sediment samples at location HZ-21 and HZ-23 were noticeably different, because of the presence of a small percentage (<3%) of calcite, cerussite ($PbCO_3$), dolomite, galena (PbS), and sphalerite (ZnS). The Pb carbonate mineral phase cerussite is a common weathering product of Pb-sulphides in high pH/pCO_2 limestone-dominated source terrains, as evidenced by Hudson-Edwards et al. (1996).

The pH of the sediment samples ranged between 5.90 and 7.34. The organic matter content, as measured by LOI, was low, with concentrations ranging between 3.0% and 4.2%. The two control sites – point HZ-0 and point HZ-A0, located, respectively, in the head of the Rookhope catchment and in the lower part of the catchment in a tributary not impacted by mining – had Pb concentrations of 97 and 825 mg kg^{-1}, respectively (Table 3). Lead concentrations in the sediment samples along the burn increased from 1610 to 15,350 mg kg^{-1}. Commonly, sediment contamination is noticeable immediately downstream from discrete point sources and decreases in a downstream direction, due to the effect of hydraulic sorting and dilution by uncontaminated sediment from tributaries (Pulford et al. 2009). However, in the Rookhope catchment, as illustrated in the GBASE sediment Pb distribution map (see Fig. 1), many tributaries, some of which are unaffected by mining, had elevated Pb contents in the sediments. The observed increased concentrations in a downstream direction, therefore, reflected both the impact of the widespread historical mining and of mineralisation. The high Pb concentrations at the control site HZ-A0 can also be related to high background values of mineralised areas.

4.3 Lead concentrations in the interstitial water of the hyporheic zone

The pore water from the stream hyporheic zone had near neutral pH except for site HZ-0, where the low pH of 4.83 reflected the peaty upland location and the more acidic bed sediments (Table 3). Full chemical analysis and selected physico-chemical parameters of the hyporheic zone pore water and overlying surface water are reported in Online Resource 1. Redox measurements indicated prevailing oxidising conditions in the hyporheic zone at the time of the sampling. This is common for bed sediments in upland reaches, where surface water–hyporheic zone exchanges are maximised due to sediment with larger particle sizes and hence higher permeability, compared to lowland rivers (Bencala 2011).

Lower concentrations of Zn together with Mn and Fe were measured in the hyporheic zone compared to surface water (Online Resource 1). This has been attributed to natural attenuation of dissolved Zn through a mechanism of precipitation/adsorption onto newly-formed manganese (Mn) and iron (Fe) oxyhydroxides on the stream bed sediments of the Rookhope Burn (Palumbo-Roe et al. 2010). Vice versa, dissolved Pb concentrations were enriched in the hyporheic zone compared to surface water and mine water samples (Fig. 3), clearly showing a distinct pattern from dissolved Mn, Fe and Zn, and possibly reflecting different metal–sediment association and/or release models. Because both surface water and mine water Pb concentrations were lower than those in the hyporheic zone, only the contaminated sediments could act as a source of dissolved Pb and account for the observed metal enrichment in the interstitial water of the hyporheic zone.

Many studies of mining-affected river sediments, both in UK and elsewhere in the world (Filipek et al. 1981; Macklin and Dowsett 1989; Byrne et al. 2010), highlight the association of Pb with Mn and Fe oxyhydroxides and indicate remobilisation of sediment-bound metals as governed by chemical sorption-desorption processes or reductive dissolution. The hyporheic zone, in particular, can be characterised by steep physico-chemical gradients highly favouring biogeochemical processes including oxidation-reduction (Benner et al. 1995). However, in this study the hyporheic zone redox conditions were shown to be too high for the Mn and Fe oxyhydroxides to become unstable (Online Resource 1) and reductive dissolution cannot be invoked to explain the high pore water Pb concentrations (up to 56 $\mu g\ l^{-1}$) at point HZ-21 and HZ-23 in the lower reaches of the Rookhope catchment, in contrast to the control sites and upstream points HZ-11 and HZ-16 (<9 $\mu g\ l^{-1}$). The lack of a similar enrichment in dissolved Mn and/or Fe in the pore water supports this conclusion.

The pore water Pb concentration of HZ-21 and HZ-23 was found close to saturation with respect to cerussite (SI_{PbCO3}= -0.56 and -0.77 for HZ-21 and HZ-23, respectively) and the mineral phase was identified by mineralogical analysis, suggesting that the Pb carbonate mineral may control the pore water concentration. Physical factors in affecting solute composition, such as the importance of particle size, need to be evaluated in future work.

The hyporheic water composition can affect downstream water quality and be significant at the catchment scale providing that sufficient connectivity between surface water and the hyporheic zone exists to allow stream–hyporheic solute exchanges (Harvey and Fuller 1998). Stream water infiltrates the shallow channel bed and banks, flows following the general gradient, and then returns to the stream with flow patterns variable in time and scale depending on variation in stream and catchment geomorphic and geologic features, such as hydraulic conductivity, alluvial volume, and streambed slope (Bencala 1984). In the case of our study catchment, the poorly sorted sandy, gravelly stream sediment would favour hyporheic flows and solute exchanges.

4.4 Lead behaviour during river bank sediment flooding

Bank sediments from sites HZ-11, HZ-16 and HZ-23 had total Pb concentrations of 1350, 975 and 29,515 mg kg^{-1}, respectively. The rate of release curve for Pb during the 88 days sediment flooding is shown in Fig. 4, with the Rookhope Burn Pb concentration used as inundation water at time zero as the starting point. The overlying water column remained oxidised during the entire period of inundation. The Eh increased with time and ranged between c. 465-550, 410-560 and 425-535 mV, for samples HZ-11, HZ-16 and HZ-23, respectively. The pH of the inundation water was immediately reduced, by c. 0.2 to 0.8 pH units, by the introduction of the Rookhope stream sediments over the first 24 hours of the study. Over the first 28 days of the inundation test, the pH of the flood water became more acidic, in general reaching a plateau after a 28 day inundation period. Sample HZ-11 had the greatest impact on the pH of the Rookhope stream water, reducing the pH by the largest amount, c. 1 pH unit in total, and maintaining a solution pH below 7 after the 28 day inundation period. Samples HZ-16 and HZ-23 maintained a pH above 7 throughout the inundation period.

The laboratory simulated flooding of river bank sediment samples from sites HZ-11, HZ-16 and HZ-23 caused a substantial increase in dissolved Pb in the overlying water column during the first day of inundation. Sediment from site HZ-23 continued to release Pb throughout. The final Pb average concentration in the water column for this sampling point was 395±12.5 μg l^{-1}. For the other sediment samples, after an initial solubilisation, a distinct dip in the amount of dissolved Pb was observed at around 28 to 60 days, after which point a further solubilisation of Pb was noted, reaching 1.1±0.1 μg l^{-1} for Point HZ-11 and 2.05±0.05 μg l^{-1} for Point HZ-16 at the end of the inundation period. The sediment pore water sampled at the end of the experiment contained Pb concentrations of 15±0.01 μg l^{-1} for Point HZ-11, 5.35±0.6 μg l^{-1} for Point HZ-16 and 491±0.1 μg l^{-1} for Point HZ-23. XRD evidence of the presence of cerussite in the sediment from sampling site HZ-23 coupled with the saturation index (close to saturation with respect to cerussite), suggested that this phase may control Pb solubility during the sediment flooding.

It is worth noticing that temporal changes in surface water pH can be substantial in metal mining-impacted catchments, as shown in the case of the adjacent Allen catchment with a fall in instream pH of approximately 1 unit between baseflow and highflow conditions (Gozzard et al. 2010), and of the Afon Twymyn in central Wales, UK, with a decreased river water pH during rain-fed flood events (Byrne et al. 2009). When estimating sediment bound-metal mobilisation during flooding, this potential decrease in surface water pH should be accounted for, due to the inverse pH-dependency of solubility of metal-bearing phases. The results of the inundation test using baseflow river water samples may underestimate the potential Pb remobilisation under field conditions. Nevertheless, these results demonstrate that the sediments can act as a significant source of dissolved Pb to the overlying water column through a diffusion mechanism, simulated in the experiment, driven by the element concentration gradients across the sediment–water interface.

5 Conclusions

In contaminated rivers and streams, reductions in surface water contamination due to metal dilution and dispersal are often observed downstream of point sources of contamination, particularly in circum-neutral and alkaline waters, such as the Rookhope Burn waters, where natural attenuation processes through chemical sorption or co-precipitation of metals like Pb are enhanced. Deviations from these decreasing trends downstream of point source pollution are due to inputs of contaminants from diffuse sources. This is the case in the

Rookhope Burn where the Pb load increased steadily down the catchment, without any apparent contribution of point sources of Pb to the stream.

The widespread contaminated bed sediments and hyporheic zone Pb-enriched pore water are considered important as a source of Pb to the water column. This study also shows the potential for diffuse flux of Pb out of the contaminated bank sediments during simulated flooding or stagnant conditions.

Characterising these diffuse contaminant sources is important for managing basins to achieve good ecological status and to optimise remediation strategies. Despite the relatively low Pb concentrations in surface water, the measured concentrations in the sediment interstitial water introduce toxic levels into the habitat for aquatic invertebrates and may thereby be a major cause of the deterioration of fish habitats in the stream, representing a significant barrier to the target of good ecological status as defined in the European Water Framework Directive.

Acknowledgments The authors would like to thank Ben Klinck and Simon Chenery for help with the sampling and analysis. This work was funded by the Natural Environment Research Council (NERC) and the paper published with the permission of the Executive Director of the British Geological Survey (NERC).

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Table 1 Hydrological setting of the sampling locations, Rookhope Burn catchment, northern England, UK

Locality Reference	National Grid Reference	Description
HZ-0	387597-545057	Peat upland. Boulders in river bed.
HZ-11	391661-542747	Alluvium. Broad stretch of river, meandering. Cobble and boulder grade gravel.
HZ-16	392747-542957	Alluvium. Straight stretch of river; minor steps in channel cobbles and boulders.
HZ-21	393809-542627	Alluvium over till. Downstream of Boltsburn Mine washing plant. Cobbles and boulders in bed. Anthropogenic influence evident. Broad.
HZ-23	394203-542016	Alluvium over till. Channel more constrained. Tree cover. Boulders in bed.
HZ-A0	394410-541554	Till over limestone. Tributary stream. Cobbles and boulders in bed of stream.

Table 2 Mass balance of dissolved lead (Pb) loads for Rookhope stream segments to the base of the catchment for the sampling events from years 2007-2009 inclusive

Stream stretch	**Net change in Pb load**		
	Jun-07 (mg s^{-1})	**Jan-08 (mg s^{-1})**	**Apr-09 (mg s^{-1})**
1-3	10.3	1.6	0.2
3-5	-2.9	0.6	0.3
5-6	2.0	1.8	-0.4
6-9	8.4	-0.5	0.2
9-11	0.8	3.3	0.1
11-13	2.9	-0.9	-0.1
13-16	-8.1	-0.9	0.3
16-19	10.5	2.9	-0.3
19-21	4.8	4.1	0.5
21-23	5.9	-3.9	0.6
23-25	9.7	8.0	0.6

Table 3 Analysis of lead (Pb) and pH of surface water, hyporheic zone pore water and bed sediments along the Rookhope Burn catchment

	Point HZ-0	Point 11/HZ-11	Point 16/HZ-16	Point 21/HZ-21	Point 23/HZ-23	Point HZ-A0
Surface water						
pH	6.22	7.02	6.87	7.33	7.25	6.88
Pb μg l^{-1}	0.96	6.15	3.78	2.80	4.56	1.37
Hyporheic zone water						
pH	4.83	7.07	6.77	7.16	6.84	6.87
Pb μg l^{-1}	4.91	8.89	4.51	55.6	43.0	3.53
Bed sediments						
pH	5.89	7.01	7.27	7.34	7.33	7.18
Pb mg kg^{-1}	96.5	1610	1978	2086	15346	825

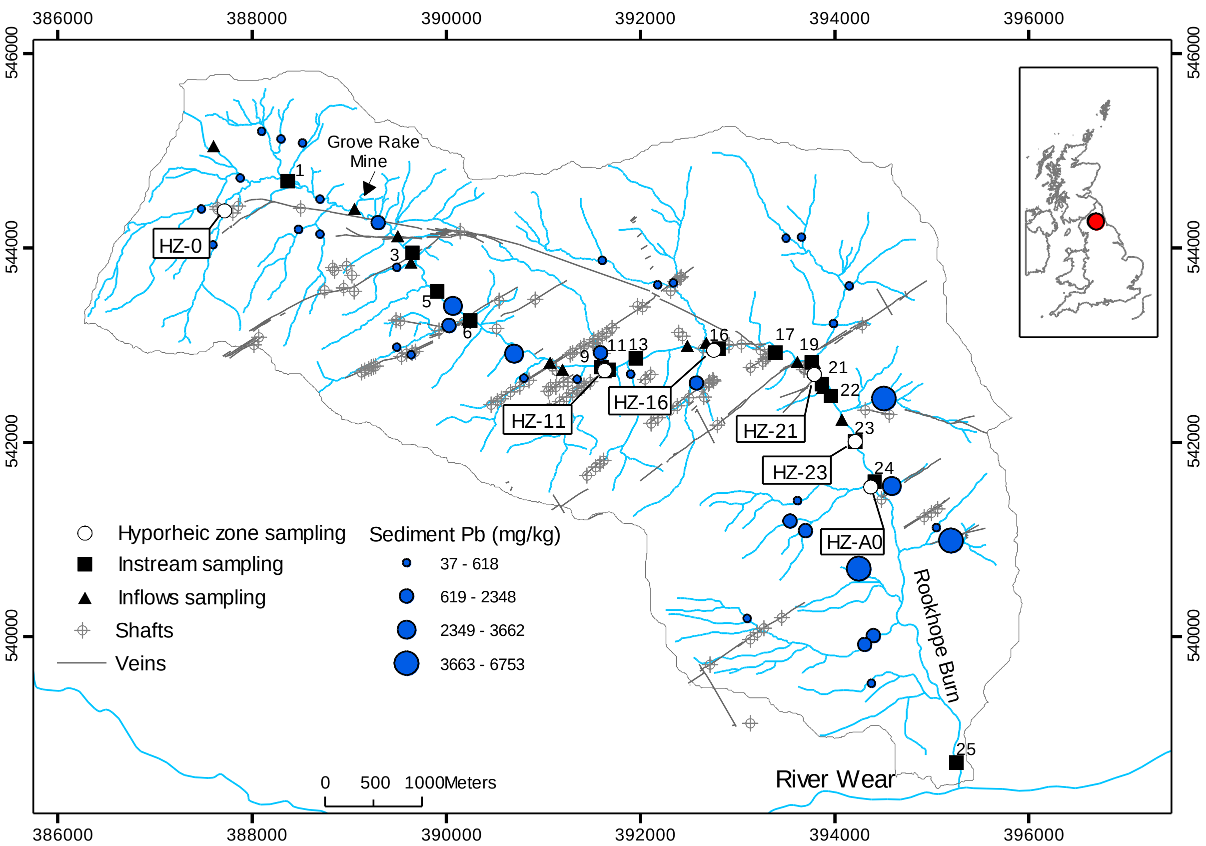
Figure captions

Fig. 1 Location map of sampling points and spatial distribution of lead (Pb) in sediments of the Rookhope Burn catchment, UK (data from British Geological Survey (BGS) Geochemical Baseline Survey of the Environment – GBASE database).

Fig. 2 Distribution of dissolved lead (Pb) concentration (µg l^{-1}) and Pb loads (mg s^{-1}) along the Rookhope Burn for three sampling events over years 2007-2009. The x-axis shows the distance from the headwaters down the catchment. Sampling points along the catchment are identified by closed square symbols. Inputs from visible point sources of Pb from contributing tributaries and mine adits are identified by closed triangles (high Pb concentrations of tributary stream receiving mine spoil seepage for June 2007 and Jan 2008 sampling events are reported against secondary y-axis with open triangle symbol).

Fig. 3 Lead (Pb) concentration distribution in the hyporheic zone (HZ) pore water (n=6), in surface water (SW) (n=6) and in mine waters (MW) (n=4) sampled in the Rookhope Burn catchment. Mine water data as reported in Banks and Palumbo-Roe (2010).

Fig. 4 Lead (Pb) release rate curves and pore water concentrations for river bank sediments at sampling points HZ-11, HZ-16 and HZ-23, with data for sample at point HZ-23 plotted on the secondary y-axis. The error bars displayed were calculated as the absolute difference between the duplicates, where the data point is the mean duplicate value.



386000
388000
390000
392000
394000
396000
546000
544000
542000
540000
Grove Rake Mine
HZ-0
HZ-11
HZ-16
HZ-21
HZ-23
HZ-A0
1
3
5
6
9
11
13
16
17
19
21
22
23
24
25
Rookhope Burn
River Wear
0 500 1000Meters
Hyporheic zone sampling
Instream sampling
Inflows sampling
Shafts
Veins
Sediment Pb (mg/kg)
37 - 618
619 - 2348
2349 - 3662
3663 - 6753

Figure 1

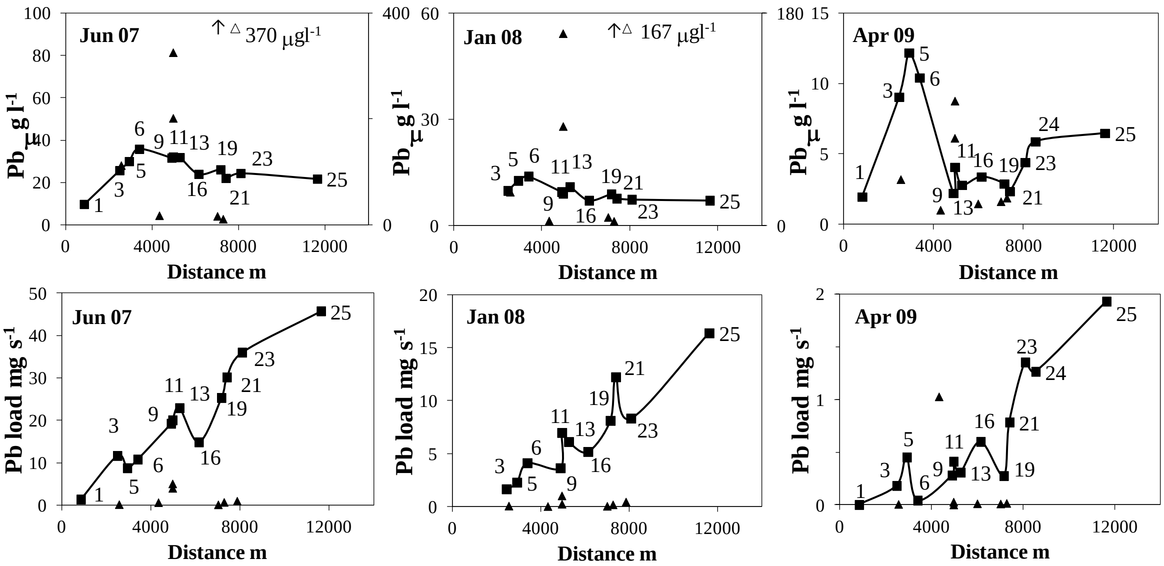
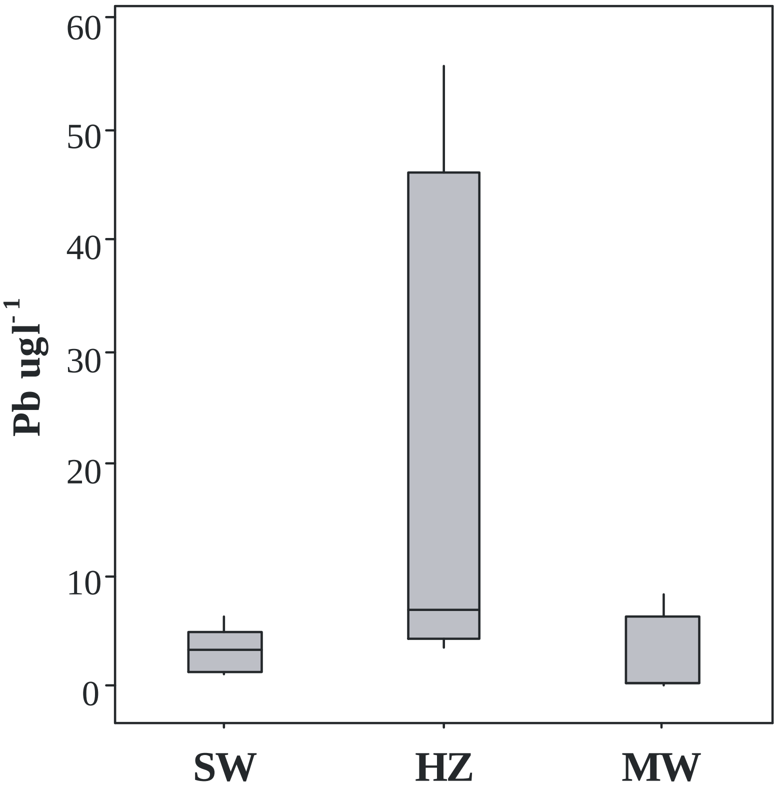

Jun 07
↑△ 370 μgl-1
Jan 08
↑△ 167 μgl-1
Apr 09
Pb μg l-1
Distance m
Pb load mg s-1

Figure 2

412



413

414 **Figure 3**

415

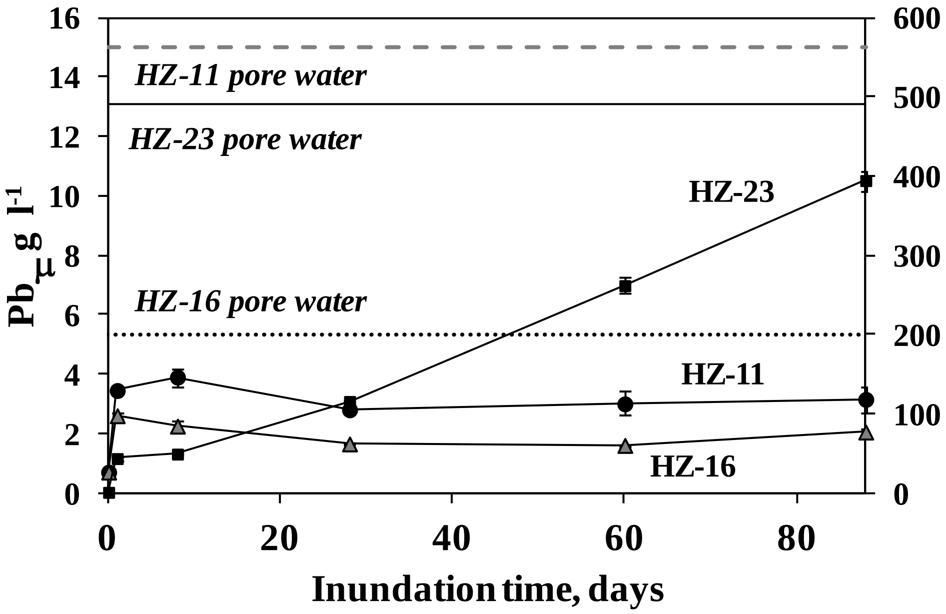

16
14
12
10
8
6
4
2
0
600
500
400
300
200
100
0
HZ-11 pore water
HZ-23 pore water
HZ-16 pore water
HZ-23
HZ-11
HZ-16
Pb μg l-1
0
20
40
60
80
Inundation time, days

Figure 4

ELECTRONIC SUPPLEMENTARY MATERIAL

IASWS 2011: THE INTERACTIONS BETWEEN SEDIMENTS AND WATER

Lead mobilisation in the hyporheic zone and river bank sediments of a contaminated stream: contribution to diffuse pollution

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Received:24 October 2011 / Accepted: 16 April 2012

Responsible editor: Geraldene Wharton

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Table ESM 1 Chemical analysis and physico-chemical parameters of hyporheic zone pore water (HZ) and overlying surface water (SW) along the Rookhope Burn on 11th May 2009

Point		T	Eh	pH	Cond	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	F^-	NPOC	Total P	Si	Ba	Sr	Mn	Total Fe	As	Cd	Cu	Ni	Pb	Zn
		°C	mV		µS cm^{-1}	mg l^{-1}															µg l^{-1}					
HZ-0	SW	9.68	349	6.22	52.0	9.68	4.58	1.27	3.74	0.557	4.91	2.78	0.051	8.82	<0.003	1.27	0.013	0.020	0.067	0.558	0.396	0.024	1.69	2.37	0.956	10.7
	HZ	10.4	406	4.83	48.0	<5.00	3.20	1.12	4.36	0.913	5.25	4.21	0.076	8.52	0.010	1.30	0.014	0.015	0.757	1.14	0.511	0.057	8.30	5.28	4.91	45.9
HZ-11	SW	9.13	268	7.02	333	65.4	43.0	7.79	7.17	3.60	9.97	75.4	2.19	3.14	<0.003	2.10	0.014	0.154	1.44	0.419	0.391	0.549	2.59	17.9	6.15	566
	HZ	9.44	257	7.07	333	71.4	42.9	8.01	7.38	4.05	10.0	73.9	2.22	2.84	0.041	2.01	0.011	0.155	0.366	0.149	0.360	0.459	3.39	12.5	8.89	472
HZ-16	SW	14.6	560	6.87	331	80.2	41.1	7.22	7.53	3.23	10.9	62.8	1.78	2.59	<0.003	1.99	0.015	0.156	0.890	0.276	0.274	0.323	1.08	10.9	3.78	269
	HZ	14.6	483	6.77	340	87.0	49.4	7.29	8.61	4.47	12.4	62.4	2.18	4.77	0.006	2.12	0.014	0.193	0.008	0.030	0.332	0.061	2.22	2.87	4.51	28.9
HZ-21	SW	9.53	456	7.33	341	96.5	45.1	7.38	9.53	3.39	11.2	60.3	1.62	2.24	<0.003	2.25	0.016	0.186	0.610	0.165	0.333	0.220	1.33	7.64	2.80	196
	HZ	10.1	423	7.16	348	99.0	45.7	7.18	9.80	3.69	12.1	62.5	1.78	2.35	0.004	2.28	0.016	0.198	0.091	0.299	0.645	0.178	4.25	4.97	55.6	82.3
HZ-23	SW	14.1	440	7.25	365	107	47.0	8.24	8.99	3.20	10.8	61.9	1.43	2.30	<0.003	2.23	0.015	0.217	0.352	0.157	0.323	0.181	1.24	5.41	4.56	117
	HZ	16.2	381	6.84	355	174	59.5	4.41	5.46	1.59	6.30	17.8	1.64	1.25	0.001	2.30	0.023	0.286	0.198	0.031	0.269	0.360	8.12	4.23	43.0	71.1
HZ-A0	SW	9.76	368	6.88	162	72.3	21.7	4.06	5.72	1.77	7.31	8.26	0.154	2.72	0.010	2.23	0.015	0.093	0.004	0.112	0.200	0.012	1.40	1.04	1.37	2.73
	HZ	10.2	471	6.87	175	70.8	22.5	3.87	5.56	1.90	7.52	8.38	0.176	2.72	0.015	2.18	0.015	0.089	0.003	0.069	0.228	0.008	2.04	1.42	3.53	2.13